JC20 Rec'd PCT/PTO 27 AUG 2001

FORM PTO-1390U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV 5-93) TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER 9052.18 U S APPLICATION NO (If known, see 37 C F R 1 5) To be assigned 09/914452
INTERNATIONAL APPLICATION NO PCT/GB00/00685	INTERNATIONAL FILING DATE February 28, 2000	PRIORITY DATE CLAIMED ~~March 4, 1999~~ FEB. 26, 1999
TITLE OF INVENTION MANAGEMENT OF MIXED WASTE RESIDUALS FROM DECONTAMINATION OF METALS		
APPLICANT(S) FOR DO/EO/US Milner et al.		

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. [ ] This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).

4. [ ] A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] has been transmitted by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).

6. [ ] A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are transmitted herewith (required only if not transmitted by the International Bureau).
   b. [ ] have been transmitted by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.

8. [ ] A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).

10. [ ] A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. [X] An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98.

12. [ ] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. [X] A FIRST preliminary amendment.
    [ ] A SECOND or SUBSEQUENT preliminary amendment.

14. [ ] A substitute specification.

15. [ ] A change of power of attorney and/or address letter.

16. [X] Other items or information: Drawings, International Search Report, International Preliminary Examination Report

JC03 Rec'd PCT/PTO 27 AUG 2001

U.S. APPLICATION NO (If known see 37 C F R 1 50)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To be assigned 09/914452	PCT/GB00/00685	9052.18

	CALCULATIONS	PTO USE ONLY
17. [ ] The following fees are submitted: **Basic National Fee (37 CFR 1.492(a)(1)-(5)):** Search Report has been prepared by the EPO or JPO . . . . **$840.00** International preliminary examination fee paid to USPTO (37 CFR 1.482). . . . . **$670.00** No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) . . . . **$690.00** Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. . . . . **$970.00** International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4). **$96.00**	**840.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$840.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$	

Claims	Number Filed	Number Extra	Rate		
Total Claims	16-20 =	0	**X $18.00**	$	
Independent Claims	1-3 =		**X $78.00**	$	
Multiple dependent claim(s) (if applicable)			**+ $260.00**	$	
TOTAL OF ABOVE CALCULATIONS =				$	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				**$840.00**	
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$	
TOTAL NATIONAL FEE =				$	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$	
TOTAL FEES ENCLOSED =				**$840.00**	
				Amount to be refunded	$
				charged	$

a. [X] A check in the amount of **$840.00** to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. ________________ in the amount of $________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0220.

NOTE: **Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

Robert J. Smith

SIGNATURE

REGISTRATION NO.: 40,820

CERTIFICATE OF EXPRESS MAILING

"Express Mail" mailing label number EL920740836US

Date of Deposit. August 27, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to Box PCT, Commissioner for Patents, Washington, DC 20231.

Keowanna V.C. Best

Date of Signature: August 27, 2001

PTO FORM-1390 (REV 5-93)

09/914452
JC03 Rec'd PCT/PTO 27 AUG 2001

Attorney's Docket No. 9052.18 PATENT #3/a

IN THE UNITED STATES DESIGNATED OFFICE (DO/US)

In re: Milner et al.
Serial No.: to be assigned
Filed: concurrently herewith
For: MANAGEMENT OF MIXED WASTE RESIDUALS FROM DECONTAMINATION OF METAL

Examiner: to be assigned
Group Art Unit: to be assigned

Date: August 27, 2001

PRELIMINARY AMENDMENT

DO/EO/US
Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to the examination of the above application and calculation of claim fees, please amend the above-identified application as indicated below. Attached hereto at page 4 is a marked-up version of the changes made to the specification and claims by the current amendment. The marked-up version of the changes is captioned "**Version With Markings To Show Changes Made**". The changes represent changes to the claims and specification from their amended form after the submission of amendments under Article 19 PCT.

In the Specification:

On page 1, line 1, please insert the following:

Cross-Reference to Related Applications

The present application is a U.S. national phase application of PCT International Application No. PCT/GB00/00685, having an international filing date of February 28, 2000 and claiming priority to United States Application Nos. 60/121,854 filed February 26, 1999 and 60/122,833 filed March 4, 1999, the disclosures of which are incorporated herein by reference in their entirety. The above PCT International Application was published in the English language and has International Publication No. WO 00/51135.

In the claims:

Please amend the claims as follows:

3. (Amended) A method according to Claim 1 wherein the calcium hydroxide and magnesium containing compound are in the form of Dolomite.

4. (Amended) A method according to claim 1 wherein the sodium hydroxide is additionally used to raise the pH of said resultant solution.

7. (Amended) A method according to claim 1 wherein caesium removal from the resultant solution is effected by addition of nickel hexacyanoferrate.

9. (Amended) A method according to claim 1 wherein a polymer is added to the resultant solution to assist settling of solids.

11. (Amended) A method according to claim 1 wherein the resultant solution is subject to UV oxidation.

13. (Amended) A method according to Claim 1 wherein the resultant solution is subjected to ion exchange to effect caesium removal.

15. (Amended) A method according to claim 1 wherein the resultant solution is subjected to mechanical filtration prior to disposal of the supernatant liquid.

REMARKS

Claims 1-16 are pending in the above application. Claims 3-4, 7, 9, 11, 13, and 15 have been amended to better conform to U.S. practice. Applicants respectfully request substantive examination on the merits.

Respectfully submitted,

Robert J. Smith
Attorney for Applicants
Registration No. 40,820

20792
PATENT TRADEMARK OFFICE

CERTIFICATE OF EXPRESS MAILING

"Express Mail" mailing label number EL920740836US
Date of Deposit: August 27, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to: Box Patent Application, Assistant Commissioner for Patents, Washington, DC 20231.

Keowanna V.C. Best
Date : August 27,2001

Version With Markings To Show Changes Made

3. (Amended) A method according to Claim 1 **[or Claim 2]** wherein the calcium hydroxide and magnesium containing compound are in the form of Dolomite.

4. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein the sodium hydroxide is additionally used to raise the pH of said resultant solution.

7. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein caesium removal from the resultant solution is effected by addition of nickel hexacyanoferrate.

9. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein a polymer is added to the resultant solution to assist settling of solids.

11. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein the resultant solution is subject to UV oxidation.

13. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein the resultant solution is subjected to ion exchange to effect caesium removal.

15. (Amended) A method according to **[any of the preceding claims]** Claim 1 wherein the resultant solution is subjected to mechanical filtration prior to disposal of the supernatant liquid.

TREATMENT OF RADIOACTIVELY CONTAMINATED METALS

FIELD OF THE INVENTION

This invention relates to the treatment of radioactively contaminated metals. For instance the present invention may be applied to the treatment of metal components which have been used in the nuclear power industry and have become radioactively contaminated. Such components can be cleaned using a combination of physical and chemical techniques following which they may be released onto the scrap metal market or melted and formed into plate or billets for recycling.

BACKGROUND OF THE INVENTION

A chemical decontamination process utilises a series of immersion tanks to remove fixed radionuclides from the surface of metal components. Acid solutions contained in these immersion tanks dissolve scale, corrosion products and some base metal to effect removal of surface contamination. The various metal species and radionuclides accumulate in the immersion tanks and, as a result, performance deteriorates and the decontaminant must be changed.

STATEMENTS OF INVENTION

The present invention provides a flexible, robust decontamination and waste treatment process enabling high throughput in a minimal cost operating regime. The process of the invention is capable of generating a significant volume of radioactive scrap metal (RSM), ranging from PWR Inconel components, which are contaminated with activation and fission products, to aluminium components contaminated with transuranics.

According to the present invention there is provided a method of treating a radioactively contaminated metal object comprising contacting the object with an acid solution to cause dissolution of a surface layer of the metal object, and raising the pH of the resultant solution with calcium hydroxide and a magnesium containing compound to cause dissolved metal to separate from the solution in solid form.

Preferably the acid is a mixture of nitric and hydrofluoric acids.

Preferably the calcium hydroxide and magnesium containing compound are provided in the form of the mineral Dolomite.

Preferably sodium hydroxide is additionally used to raise the pH of the resultant solution. More preferably the sodium hydroxide is added after the calcium hydroxide and until the pH is raised to from 9 to 11, more preferably to about 9.5.

Preferably caesium removal from the resultant solution is effected by addition of nickel hexacyanoferrate. It is preferred that the nickel hexacyanoferrate is prepared "fresh *in situ*", that is to say immediately or shortly before addition to the resultant solution. This avoids degradation of the nickel hexacyanoferrate which decomposes on storage.

Preferably, a polymer is then added to assist settling of solids. More preferably, the polymer is an anionic polymer.

Preferably the resultant solution is subjected to UV oxidation, more preferably by adding sodium hypochlorite and subjecting the solution to UV radiation.

Preferably the resultant solution is subjected to ion exchange using the material clinoptillolite, a natural zeolite, in order to remove caesium not already removed by the nickel hexacyanoferrate treatment.

Preferably the resultant solution is subjected to mechanical filtration prior to disposal of the supernatant liquid.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 of the accompanying drawings is a flow diagram of a decontamination process in accordance with the present invention. As indicated in Figure 1, the process involves various unit operations. The incoming radioactive scrap (RS) is subjected to segregation and size reduction. It is then sentenced for physical chemical decontamination. Processing takes place through the decontamination line and a radionuclide contamination survey of the processed metals is carried out. The decontaminated metals are sent for recycling, disposal as LLW or sale into the scrap market. The spent decontamination liquor is treated and this results in solid/liquid separation. The process liquors are treated to meet the local sewer discharge limits. Process sludges are immobilised for disposal as non-RCRA dry active waste.

It is of importance in the context of the present invention that the chemical decontamination stage or stages provide a safe and cost effective process for the decontamination of RSM. The chemical decontamination should be capable of accepting a wide variation in feedstock and offer a cost saving over direct disposal of RSM. There should be produced a minimal volume of non RCRA secondary waste and the process liquors should be suitable for discharge to the local sewer.

Preferably the acid solution providing the decontamination of liquor comprises nitric and hydrofluoric acids which enable decontamination to be carried out on a varied or variable feedstock at high throughput levels. The aggressive nature of the nitric/hydrofluoric acid decontamination process requires careful control of the process parameters to achieve an optimum surface corrosion rate for a given substrate. Such optimising has various advantages. Base metal corrosion is kept to a minimum. The lifetime of the decontamination tank or tanks is prolonged. Uniform surface corrosion takes place without pitting of the base metal. The volumes of secondary waste are minimised by avoiding dissolution of uncontaminated base metal. There is also an avoidance of uncontrolled dissolution reactions which gives rise to off gases as the acids break down.

In order to achieve the optimal surface corrosion rate for a varied feedstock using a single chemical decontaminate, there is required a careful control of the temperature of the decontamination tank, the concentrations of the mixed acid treatments solution, the agitation and the oxidation potential of the decontaminant, the concentration of the dissolved metals and radionuclides in the decontamination tanks and the sequencing and immersion time in the decontamination tanks.

As fresh acid solution contacts a contaminated metal surface, dissolution occurs and the metal is dissolved in the acid solution. This results in metal loading of the acid bath. Although the reaction of the acids upon the metal surface is complex and involves a number of equilibrium reactions, the dissolution of iron by nitric acid can be simplified to the following reaction:-

$$Fe^{2+} + 2HNO_3 = Fe(NO_3)_2 + 2H^+ \text{ and } Fe^{2+} + 2HF = FeF_2 + 2H^+$$

Similar reactions take place with other metals such as:-

$$Cr^{3+} + 3HNO_3 = Cr(NO_3)_3 + 3H^+$$
$$Fe^{3+} + 3HNO_3 = Fe(NO_3) + 3H^+$$
$$Al^{3+} + 3HF = AlF_3 + 3H^+$$
$$Ni^{2+} + 2HF = NiF_2 + 2H^+$$

In the case of the dissolution of iron by nitric acid, there is a theoretical requirement for two moles of nitric acid to dissolve one mole of iron. However due to passivation of the metal surface, plate-out, oxidation of iron and the extremely slow dissolution rate as the acid is consumed in the dissolution reactions, such metal loading is impractical.

As a first order approximation, the metal dissolution rate of the acids is directly proportional to the concentration of the acids. Accordingly, for a high throughput of metal in the decontamination line, two factors have a significant impact on

decontamination performance. First, the overburdening of the acids with dissolved metals results in insufficient unreacted acid to achieve significant dissolution of the metal substrate. Secondly unreacted acid in the spent liquor has to be neutralised during waste treatment and this generates a significant volume of secondary waste.

Accordingly, the operation of the decontamination process of the present invention has involved a balance which has been struck between metal loading of the acids and dissolution rates, taking into account the potential for surface pitting and off gas production. It is important to minimise the production of off gasses that require scrubbing, thereby resulting in the generation of a secondary waste form and depletion of the acid capacity. This is particularly important when decontaminating the more reactive metals such as carbon steel and aluminium.

In order to obtain the optimisation mentioned above, it is preferred that the process is operated using a plurality of decontamination tanks in a manner referred to as "lag" basis. This procedure involves designating the decontamination tanks as low, medium and high dissolved metal content, each fulfilling a particular duty within the overall decontamination process. The low tank is used for final polishing of the decontaminated metal as this tank has the lowest radionuclide inventory and the highest dissolution kinetics. The high tank is used for initial decontamination where the highest levels of radionuclides, associated with the outermost surface, are removed. The medium tank is a transitional tank which is additionally used for "special" materials, which are substantially different from other materials of the feedstock. The use of the medium tank is optional.

During the process, the tanks are rotated from low to high based on a predetermined dissolved metal and radionuclide inventory. The high tank is taken off line and designated as spent once decontamination has become ineffective. In order to establish this there is carried out a regular sampling and analysis procedure to measure and record trends in tank performance. The procedure may be simplified with the cost of analysis reduced by using the experience gained from operating the

process to devise a "finger print" which can be used to determine when a tank should be reclassified.

The operational flexibility of the chemical decontamination line allows both decontamination for recategorisation to LLW and also to free release. The economic case for free release or recategorisation has to be considered. In the case of a PWR primarily loop component which has been exposed to a high temperature, high pressure liquid environments generally require the removal of 20 to 30μm of corrosion film and base metal to achieve recategorisation to LLW. Achieving free release levels can require the removal of an additional 150 to 200μm of metal. Components from fuel cooling pools such as stainless fuel racks can be decontaminated to LLW by removing 5 to 8μm surface and free release can be achieved by removing 15μm of surface metal. The less demanding metal removal could favour free release.

The tank lag system allows decontamination to free release to be performed in the low activity tank and decontamination for recategorisation to LLW to be performed initially in the high and subsequently in the medium activity tank.

An additional advantage of the lag system is the degree of uniformity, in terms of dissolved metal and radionuclide content, that is introduced to the spent tank waste treatment process.

The spent acid resulting from the decontamination stage or stages may be subjected to a number of treatment steps. Treatment of the spent acids produces two waste streams. One is an alkaline wastewater which, after final polishing by chelant oxidation followed by ion exchange, is discharged to the local sewer. The other is a sludge containing the major metal species (iron, chromium, nickel) and radionuclides (cobalt, cesium) which may be directly solidified by grouting with, for instance, Portland cement to meet the appropriate waste acceptance criteria.

The spent acids from the chemical decontamination process contain a high concentration of dissolved metals and radionuclides, as illustrated in the following table:

Contaminant	Cr	Ni	Fe	Cu	^{60}Co	$^{134/137}Cs$	^{241}Am ^{54}Mn	Anions (nitrate fluoride chloride)
Concentration	1600 mg/L	2000 mg/L	12,500 mg/L	2000 mg/L	80,000 pCi/L	3000 pCi/L	1000 pCi/L	>10%

In treating the spent acids solution, the aim is to produce a minimal volume of non-RCRA solid waste. Since the composition of the metal component which is treated in the chemical decontamination stage affects the ratios of metals in the spent acid, a highly flexible approach is required. The waste treatment process may be either a batch process or a continuous process although reference will be made hereinafter to a batch process.

The waste treatment process may involve various steps as illustrated in Figure 2 of the accompanying drawings. As illustrated the spent acids solution is partially neutralised and conditioned using calcium hydroxide. The pH is then adjusted to a value in the range of from 9 to 10 using sodium hydroxide. Flocculation is then effected by seeding with inorganic adsorbents causing resultant coprecipitation of metals and radionuclides. Polymers are then added to aid gravity settling of solids. The solids and liquid are then separated and the solids are subjected to grouting. The wastewater liquid is then treated by means of UV/sodium hypochlorite to cause oxidation of chelate. Finally the waste water is polished by ion exchange using clinoptillolite as the resultant liquid is discharged to a local sewer.

The above described process steps may be performed sequentially over a 24 hour period and the acid tank. when empty, is replenished with fresh acid and returned to service. The above described treatment process is both robust and simple to operate and uses readily available, low cost chemicals and process equipment.

Calcium hydroxide is used principally to condition the metal hydroxide floc by assisting in the binding of leachable metals, principally chromium. Use of the magnesium containing compound improves the removal of hexavalent chromium. The calcium fluoride formed in the partial neutralisation forms the body of the floc and improves sludge settling characteristics. The calcium hydroxide is not used for pH control as this may result in the formation of an excessive amount of calcium sludge requiring disposal as a secondary waste product. Accordingly pH adjustment is carried out using sodium hydroxide, which is highly soluble and results in a sharp inflection point in pH, thereby allowing greater process control. The calcium hydroxide and the sodium hydoxide may be added together or in either order.

In the case where the acid includes hydrofluoric acid, the calcium from the calcium hydroxide forms insoluble calcium fluoride, making downstream processing of the supernatant liquid easier since the fluoride has been removed.

The presence of dissolved iron assists in chromium removal due to the Fe (II)↔Fe (III) couple ensuring the chromium is present in reduced Cr (III) state. In some cases, when the Fe (II)/Cr ratio in the spent acid is less than 4:1 wt/wt, additional ferrous iron may be required to reduce chromium to the less soluble form. This can also be controlled by management of the processing of nickel/chromium alloys and stainless or carbon steels in order to supply the appropriate iron ratio needed for chromium reduction.

The above described two-stage neutralisation results in the formation of a floc which contains virtually all the radionuclide and metal contaminants with the exception of cesium which is highly soluble. Typically cesium is removed from the wastewater by means of an ion exchange column. However such an approach has a number of disadvantages. The processing is slow due to the slow kinetics of the reactions. The highly selective ion exchange media which is required for column use in high salt streams is expensive. Less selective ion exchange media were rapidly exhausted by other metals and radionuclides, producing excessive secondary waste. Pretreatment

to remove particulate which has the potential to bind the columns is required and this produces an additional waste stream.

In a preferred method according to the present invention, cesium removal is affected using nickel hexacyanoferrate (HCF). A solid HCF ion exchanger is added in the amount of 300 ppm as a dilute slurry directly into the batch treatment tank once the pH has been adjusted. Caesium removal is aided by isotopic dilution by adding 10 ppm of non-radioactive caesium chloride. Preferably the HCF is used immediately after it has been formulated. Lower caesium removal and higher residual nickel resulted if the HCF is aged.

The kinetics of the cesium complexation with HCF is very rapid and the complex formed is removed from solution by adsorption and agglomeration with the metal hydroxide floc. A decontamination factor of 600 has been achieved for cesium and the supernant liquor was free of all metals except a few ppm of nickel and chromium and trace levels of caesium. Final caesium removal was accomplished by adsorption on clinoptillolite, a natural zeolite.

Separation of the floc from the supernatant can be achieved by the use of mechanical separation devices. However such devices are either costly, generate a secondary waste in the form of a filter media or require frequent manual intervention. Accordingly it is preferred to make use of gravity settling and decanting. In order to speed the stages of the process, several hundred ppm of an anionic polymer was added to increase the rate of settling and the clarity of the supernatant. More preferably, the tank content are rotated using a stirrer device.

After a period of 4 to 8 hours the supernatant from the HCF step was decanted and processed through the waste water treatment polishing step. The solution was dosed with 0.25 to 0.5% sodium hypochlorite and treated with UV light to oxidise the soluble heavy metal complexes (nickel and cobalt-60). Insoluble compounds are produced. The treatment time was from 6 to 18 hours. The particulate is removed by

mechanical filtration by passing the material through a bed of sand and charcoal followed by cartridge filters.

As a result the concentration of heavy metals, primarily nickel, is reduced from 10 to 20 mgL to the required discharge limit of not greater than 1.5 mg/L. The ^{60}Co was similarly reduced from 20 to 50 pCi/L to the required discharge limit of less than 1 pCi/L.

If necessary, further caesium removal may be achieved by mixing the decant liquor with laundry water from the final effluent tank. This dilution lowered the concentration of nitrate and fluoride salts in the wastewater and improved the efficiency of the caesium removal by ion exchange using two columns packed with clinoptillolite. The clinoptillolite column had a residence time of 60 to 80 minutes and the resulting wastewater met local discharge criteria. The capacity of the ion exchange column was found to be between 80,000 to 90,000 bed volumes and the sand bed filter did not require to be changed out.

The second waste stream from the WTS comprises the radionuclide and metal contaminated sludge from the settling and decanting step. This sludge or metal floc was directly solidified in a cementicious grout. This was achieved by pumping the settled solids from the batch treatment tank into 250 litre (55-gallon) drums. A helical drum mixer was used to incorporate 0.75 to 1.0 kg of portland cement per kg of sludge. This was accomplished with 20 to 30 minutes mixing and there was only a small heat rise during this process. The grout was then pumped from the drums into moulds that were designed to produce a final waste form meeting local acceptance criteria for size requirements for debris. The resulting grouted waste was produced with a minimal volume increase of 20%. It was cured overnight with no bleed and had a strength of over 345 k Pa (50 psi).

Aspects of the present invention will now be described, by way of illustration only, in the following example.

A quantity of radioactively contaminated ferrous iron was loaded into a bath contain nitric and hydrofluoric acids and the acids were allowed to react with the surface of the iron until a desired metal loading in the bath had been achieved. Dolomitic lime (calcium hydroxide containing magnesium) was added to the bath in the form of a water slurry. The bath was then agitated for 30 minutes following which caustic soda (sodium hydroxide diluted with water) was added to give a pH in the bath of 9.5. The bath was agitated for a further 30 minutes following which caesium removal is effected by the addition of nickel hexacyanoferrate (HCF). The HCF was prepared "fresh *in situ*" to avoid degradation in storage, that is to say, it is added to the bath immediately after its preparation.

At this stage an anionic polymer (Nalclear) was added to the bath in order to promote the settling of the solids over a period of about 12 hours. The resultant solid sludge was separated from the supernatant and was immobilised in grout.

The supernatant was then treated with sodium hypochlorite which was added continuously while the bath was subjected to UV light radiation. At a pH of 9.5 solid nickel complexes are formed and removed by mechanical filtration. The pH was adjusted to 11.5 in order to remove solid cobalt complexes.

The resultant liquid may be treated by clinoptillolite ion exchange to remove further caesium, following which the liquor may be discharged to a sewer.

CLAIMS

1. A method of treating a radioactively contaminated metal object comprising contacting the object with an acid solution to cause dissolution of a surface layer of the metal object, and raising the pH of the resultant solution with calcium hydroxide and a magnesium containing compound to cause dissolved metal to separate from the solution in solid form.

2. A method according to Claim 1 wherein the acid is a mixture of nitric and hydrofluoric acids.

3. A method according to Claim 1 or Claim 2 wherein the calcium hydroxide and magnesium containing compound are in the form of Dolomite.

4. A method according to any of the preceding claims wherein the sodium hydroxide is additionally used to raise the pH of said resultant solution.

5. A method according to Claim 4 wherein the sodium hydroxide is added after the calcium hydroxide and until the pH is raised to from 9 to 11.

6. A method according to Claim 5 wherein the pH is raised to about 9.5.

7. A method according to any of the preceding claims wherein caesium removal from the resultant solution is effected by addition of nickel hexacyanoferrate.

8. A method according to Claim 7 wherein the residual hexacyanoferrate is prepared shortly before addition to the resultant solution.

9. A method according to any of the preceding claims wherein a polymer is added to the resultant solution to assist settling of solids.

10. A method according to claim 9 wherein the polymer is an anionic polymer.

11. A method according to any of the preceding claims wherein the resultant solution is subjected to UV oxidation.

12. A method according to Claim 11 wherein the UV oxidation is carried out by adding sodium hypochlorite and subjecting the solution to UV radiation.

13. A method according to any of the preceding claims wherein the resultant solution is subjected to ion exchange to effect caesium removal.

14. A method according to Claim 13 wherein the ion exchange is carried out using clinoptillolite.

15. A method according to any of the preceding claims wherein the resultant solution is subjected to mechanical filtration prior to disposal of the supernatant liquid.

16 A method according to Claim 1 wherein the acid solution comprises nitric and hydrofluoric acids and the treatment with calcium hydroxide and a magnesium containing compound is followed by addition of nickel hexacyanoferrate and by further subjecting the resultant solution to UV oxidation.

P15734.1

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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60/122,833	4 March 1999 (04.03.99)	US

(71) Applicant *(for all designated States except US)*: BRITISH NUCLEAR FUELS PLC [GB/GB]; Risley, Warrington, Cheshire WA3 65AS (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: MILNER, Timothy, N. [GB/GB]; British Nuclear Fuels plc, Derwentwater Pavilion, Westlakes Science and Technology Park, Moor Row, Cumbria CA24 3JX (GB). ROBBINS, Rebecca, A. [GB/GB]; Bristish Nuclear Fuel plc, Derwentwater Pavilion, Westlakes Science and Technology Park, Moor Row, Cumbria CA24 3JX (GB). HOLMES, Robert, G., G. [GB/GB]; British Nuclear Fuel plc, Derwentwater Pavilion, Westlakes Science and Technology Park, Moor Row, Cumbria CA24 3JX (GB). SHEALY, Stuart [US/US]; IT Corporation, Knoxville, TN (US). MORREN, Edward [US/US]; IT Corporation, Knoxville, TN (US). AUSTIN, Colin, R. [US/US]; MSC, Oakridge, TN (US).

(74) Agent: HARRISON GODDARD FOOTE; Tower House, Merrion Way, Leeds LS2 8PA (GB).

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(54) Title: TREATMENT OF RADIOACTIVELY CONTAMINATED METALS

(57) Abstract

Radioactively contaminated metal objects are treated with an acid solution to cause dissolution of a surface layer of the objects. The pH of the solution is then raised with calcium hydroxide and a magnesium containing compound to cause dissolved metal to separate from the solution in solid form. Further treatment steps may include addition of sodium hydroxide and nickel hexacyanoferrate, polymer assisted settling of solids, UV oxidation, ion exchange and filtration.

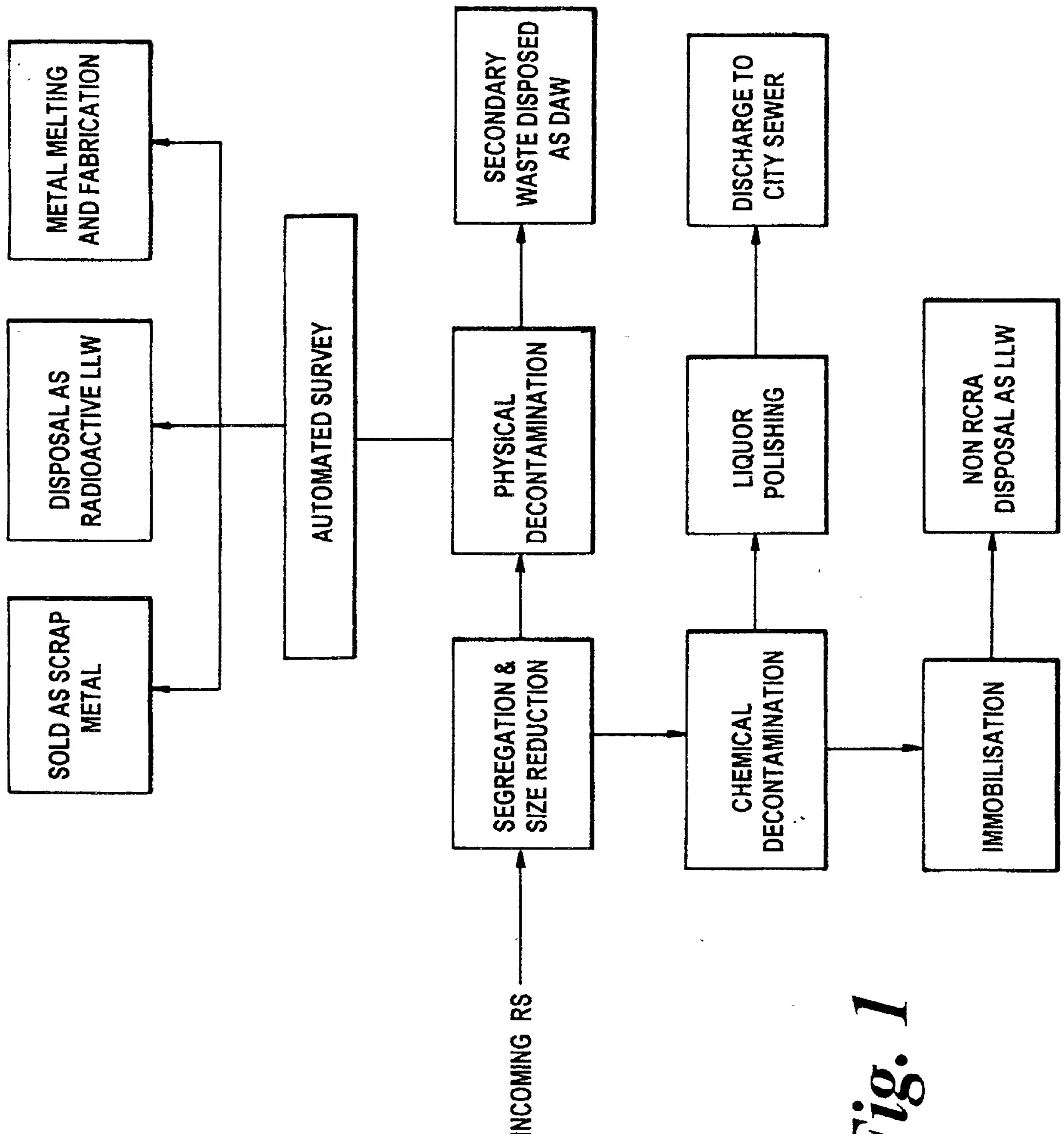
METAL MELTING AND FABRICATION
DISPOSAL AS RADIOACTIVE LLW
SOLD AS SCRAP METAL
AUTOMATED SURVEY
SECONDARY WASTE DISPOSED AS DAW
PHYSICAL DECONTAMINATION
SEGREGATION & SIZE REDUCTION
INCOMING RS
DISCHARGE TO CITY SEWER
LIQUOR POLISHING
CHEMICAL DECONTAMINATION
NON RCRA DISPOSAL AS LLW
IMMOBILISATION

Fig. 1

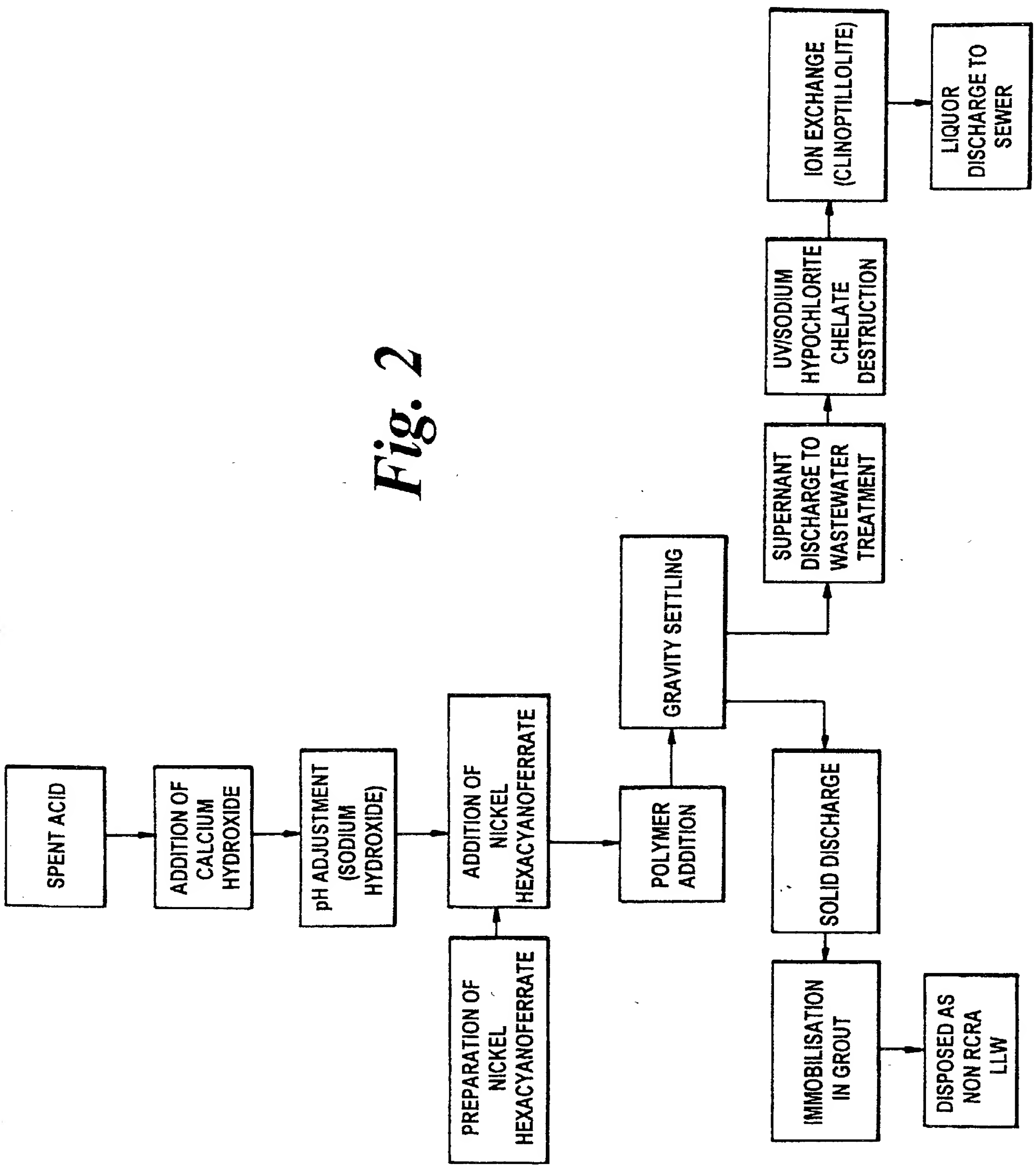
SPENT ACID
ADDITION OF CALCIUM HYDROXIDE
pH ADJUSTMENT (SODIUM HYDROXIDE)
ADDITION OF NICKEL HEXACYANOFERRATE
PREPARATION OF NICKEL HEXACYANOFERRATE
POLYMER ADDITION
GRAVITY SETTLING
SUPERNANT DISCHARGE TO WASTEWATER TREATMENT
UV/SODIUM HYPOCHLORITE CHELATE DESTRUCTION
ION EXCHANGE (CLINOPTILLOLITE)
LIQUOR DISCHARGE TO SEWER
SOLID DISCHARGE
IMMOBILISATION IN GROUT
DISPOSED AS NON RCRA LLW

Fig. 2

09/914452 .082102 #6

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Attorney Docket No. 9052-18

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled **MANAGEMENT OF MIXED WASTE RESIDUALS FROM DECONTAMINATION OF METALS,**

the specification of which

☐ is attached hereto

OR

☒ was filed on August 27, 2001 as United States Application No. 09/914,452.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

PCT/GB00/00685	PCT	2/28/2000	☒ Yes ☐ No
Number	Country	MM/DD/YYYY Filed	Priority Claimed
			☐ Yes ☐ No
Number	Country	MM/DD/YYYY Filed	Priority Claimed
			☐ Yes ☐ No
Number	Country	MM/DD/YYYY Filed	Priority Claimed

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

60/121,854	02/26/1999
Application Number(s)	Filing Date (MM/DD/YYYY)
60/122,833	03/04/1999
Application Number(s)	Filing Date (MM/DD/YYYY)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application (37 C.F.R. § 1.63(d)).

Appln. Serial No.	Filing Date	Status Patented/Pending/Abandoned

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following registered attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

Customer Number

20792

PATENT TRADEMARK OFFICE

Send correspondence to: David D. Beatty
Myers Bigel Sibley & Sajovec
Post Office Box 37428
Raleigh, NC 27627

Direct telephone calls to: David D. Beatty
(919) 854-1400

Facsimile: (919) 854-1401

1-00 Full name of first joint inventor: **Timothy Nicholas Milner**

Inventor's Signature: ______________ Date: 26th APRIL 02

Residence: Centreville, Virginia VA

Citizenship: Great Britain

Post Office Address: 13232 Maple Creek Lane
Centreville, Virginia 20120

2-00

Full name of second joint inventor: **Robert George Godfrey Holmes**

Inventor's Signature: Bob Holmes Date: 23 April 2002

Residence: Idaho Falls, Idaho ID

Citizenship: Great Britain

Post Office Address: 2428 St Clair Road
Idaho Falls, Idaho 83404

3-00

Full name of third joint inventor: **Rebecca Robbins**

Inventor's Signature: ________ Date: 4-30-02

Residence: Idaho Falls, Idaho ID

Citizenship: Great Britain

Post Office Address: 3420 Creekside Drive
Idaho Falls, Idaho 83404

Charles CEM 4/23/02

Full name of fourth joint inventor: **Edward Morren**

Inventor's Signature: CEMorren Date: 4/23/02

Residence: Seymour, Tennessee

Citizenship: USA CEM 4/23/02 ~~Great Britain~~

Post Office Address: 619 Burnette Station Road
Seymour, Tennessee 37865

09994952 .052102

5-00 Full name of fifth joint inventor: **Stuart Shealy**

Inventor's Signature: ______________ Date: 22 April 2002

Residence: Farragut, Tennessee TN

Citizenship: ~~Great Britain~~ USA GBS 4/22/2002

Post Office Address: 11804 North Monticello Drive
Farragut TN 37922

6-CO Full name of sixth joint inventor: **Colin Austin**

Inventor's Signature: ______________ Date: 10 MAY 02

CR AUSTIN

Residence: Fairfax, Virginia VA

Citizenship: Great Britain

Post Office Address: BNFL Inc
Suite 450
10306 Eaton Place
Willow Wood Plaza
Fairfax, Virginia 22030